DE82000821
BDX-613-2643

Shelf Life Determination of an Epoxy Resin by Accelerated Aging

By H. M. Smith

Published September 1981

Final Report

Prepared for the United States Department of Energy
Under Contract Number DE-AC04-76-DP00613.

Bendix
Kansas City
Division

Printed in the United States of America

Available From the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, Virginia 22161.

Price: Microfiche $3.00
Paper Copy $4.50

BDX-613-2643
Distribution Category UC-25

SHELF LIFE DETERMINATION OF AN EPOXY RESIN BY ACCELERATED AGING

By H. M. Smith

Published September 1981

Final Report
H. M. Smith, Project Leader

Project Team:
A. V. May
C. L. Long

Technical Communications

Bendix Kansas City Division

SHELF LIFE DETERMINATION OF AN EPOXY RESIN BY ACCELERATED AGING

BDX-613-2643, Final Report, Published September 1981

Prepared by H. M. Smith

The aging characteristics of GE-100, a German manufactured equivalent of Shell's Epon 812 epoxy resin, were determined by an accelerated aging study. The changes induced in the GE-100 by thermal aging were observed at five elevated temperatures over a period of three months. Analysis of the data permitted a prediction of the changes expected during shelf storage of the resin at 4.4, and at 25°C. Test samples of Ablefoam Number 5, prepared from GE-100 resin thermally aged the equivalent of 11.5 years at 4.4 and at 25°C, met all requirements. The results indicate that the GE-100 resin has a shelf-life exceeding 11 years at cold storage and at ambient conditions.

DJC/js

The Bendix Corporation
Kansas City Division
P. O. Box 1159
Kansas City, Missouri 64141

A prime contractor with the United States Department of Energy under Contract Number DE-AC04-76-DP00613

CONTENTS

ILLUSTRATIONS

TABLES

SUMMARY

Shell's Epon 812 epoxy resin is a critical component of Ablefoam Number 5, a foam encapsulant. Because Shell recently removed Epon 812 from the market, a search for an alternate supply of an Epon 812 equivalent was conducted. GE-100, a German manufactured resin, was found to be chemically equivalent to Epon 812 and at present commercially available. Because of uncertainties about future availability, consideration is being given to a one-time purchase of all necessary resin. Thus, the question of the shelf-life of GE-100 naturally arises.

A three-month thermally accelerated aging study of the GE-100 resin was performed. The objectives were to define the mode and rate of degradation under cold storage (4.4°C), and ambient storage conditions, and then to use resin aged the equivalent of at least 10 years at the two storage conditions to prepare samples of Ablefoam Number 5 for testing.

Samples of the resin were aged at 50, 70, 85, 100, and 120°C for up to three months. The aging parameters measured to follow changes induced by thermal aging were kinematic viscosity, epoxide equivalent weight, and, qualitatively, molecular weight changes by gel permeation chromatography. The mechanism of degradation of the resin was found to be homopolymerization, as evidenced by increases in viscosity, epoxide equivalent weight, and average molecular weight. Equations were developed that quantitatively describe the changes in viscosity and epoxide equivalent as functions of time and temperature. From these equations and the Arrhenius equation, the degree of aging to be expected at the two storage conditions was calculated.

Two of the aged resin samples were used to prepare test specimens of Ablefoam Number 5. One sample had been aged the equivalent of 11.5 years at 4.4°C, and the other aged the equivalent of 11.5 years at 25°C. The Ablefoam Number 5 specimens prepared were tested for compressive strength at 93°C and at room temperature. The results were compared with the requirements and with results from foam prepared from unaged GE-100 resin. The testing results indicate that while the aged samples gave lower compressive strengths than the unaged sample, the values easily exceeded minimum requirements.

The aging study has shown that GE-100 resin may be purchased and successfully stored for the required time.

DISCUSSION

SCOPE AND PURPOSE

Shell's Epon 812 epoxy resin is a critical component in the forma-tion of Ablefoam Number 5, a foam encapsulant. The Ablefoam Number 5 formulation is supplied to Bendix by the Ablestik Corporation. In September 1979, Ablestik informed Bendix that Shell had withdrawn Epon 812 from the market. A search, therefore, for an alternate supply of an Epon 812 equivalent was conducted. The search indicated that a resin chemically equivalent to Epon 812 is manufactured in Germany as GE-100 by Raschig GmbH, and marketed in the United States by Howard Hall International. Foam formulation tests proved that the German GE-100 is in fact equivalent to Epon 812 for the preparation of the Ablefoam Number 5.

Concern over the continued availability of the resin both by Sandia National Laboratory Albuquerque (SNLA), and Bendix led to consideration of purchasing the entire amount needed from Howard Hall International. To do this, some assurance that the material could be stored without serious degradation was required. After consultation with Sandia, it was agreed that Bendix would perform a three-month accelerated aging study on the German GE-100 resin. Aging properties and rates would be determined at five elevated temperatures. Then, samples known to be aged the equivalent of 10 to 11 years at cold storage (4.4°C), and at ambient temperature (25°C) would be formulated into Ablefoam Number 5 and tested for conformance with requirements. This report presents the results of the GE-100 accelerated aging study.

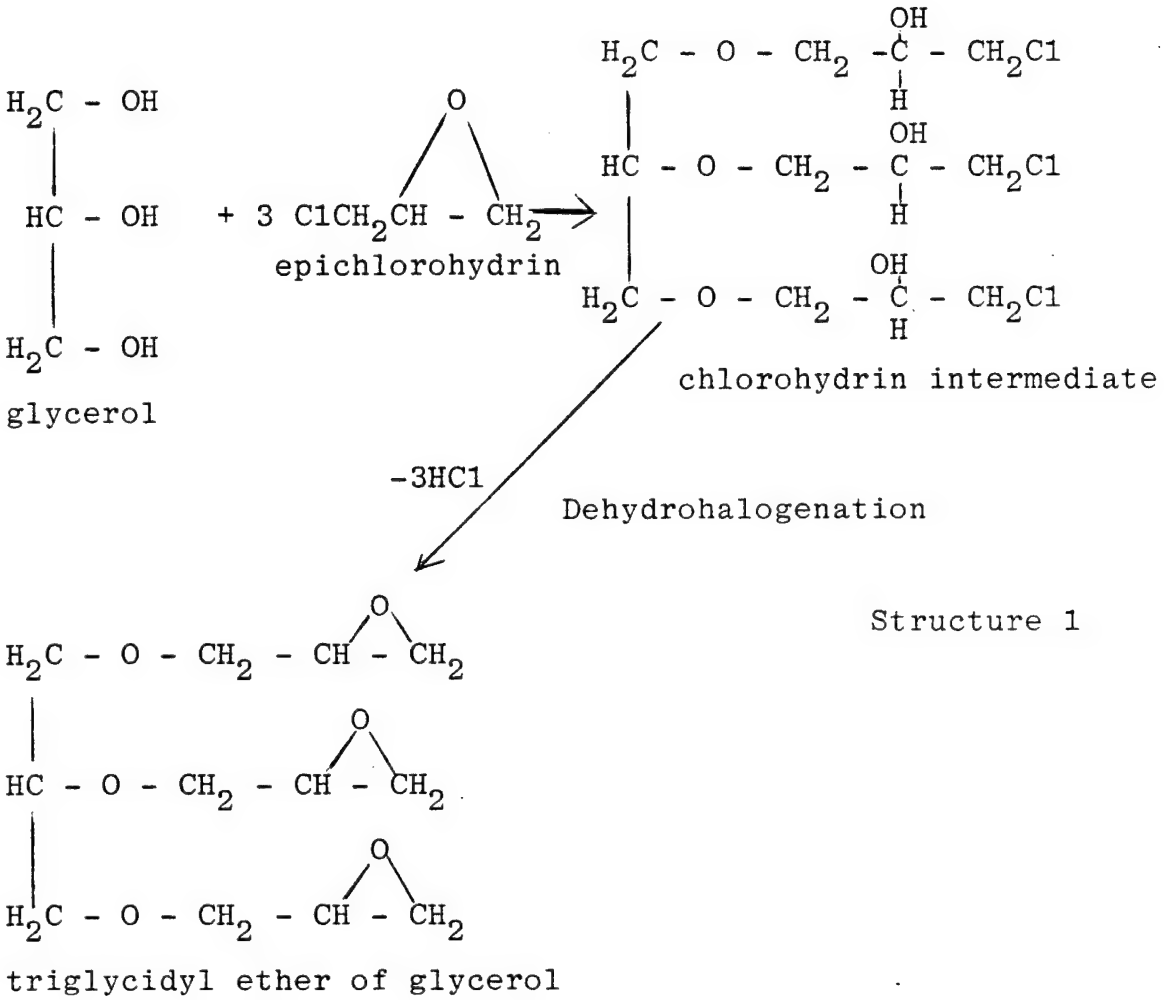
PRIOR WORK

No work on this subject has been conducted previously at Bendix Kansas City.

ACTIVITY

Chemical Properties of the Resin

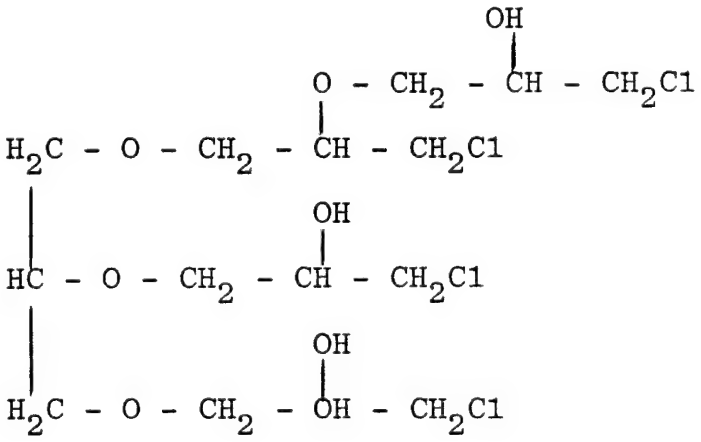
Shell's Epon 812, or the German GE-100 equivalent, is the triglycidyl ether of glycerol.[1] It is synthesized in two steps: glycerol is first reacted with epichlorohydrin to produce a chlorohydrin intermediate which is then dehydrohalogenated by sodium aluminate or the like.[1] The reaction scheme follows.



Structure 1

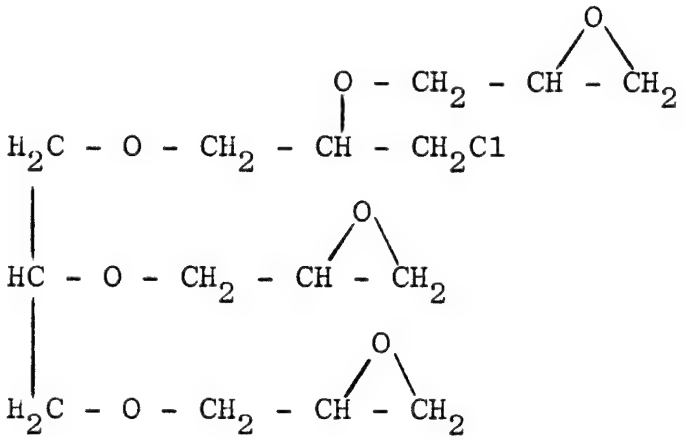
triglycidyl ether of glycerol

The idealized synthesis illustrated in reaction 1 is in fact not realized in practice. The hydroxyl group of the chlorohydrin intermediate reacts with epichlorohydrin at about the same rate as glycerol. Thus, higher molecular weight species such as the following example can be formed.



Structure 2

When this intermediate undergoes dehydrohalogenation, a chlorine-containing triepoxy results.



Structure 3

Many such chlorine-containing oligomers can be formed, and the greater the molecular weight, the more chlorine atoms the molecule will contain.

A gel permeation chromatograph of the commercial GE-100 resin is shown in Figure 1. The largest peak at an elution volume of 26 was identified by mass spectrometry as the molecular species shown in Structure 3. The peak at an elution volume of 28 is assumed to be the idealized material shown in Structure 1. The peaks at elution volumes below 26 are higher molecular weight species containing two or more chlorine atoms per molecule.

The commercial product is a mixture of several molecular species. The resin, whether Epon 812 or GE-100, has an advertised average molecular weight of 306, an epoxide equivalent weight of 145 to 160, and a chlorine content of 10 to 12.5 percent. Analysis at Bendix showed that chloride ion content was 40 ppm.

Experimental Design

The experimental design to estimate the storage lifetime of GE-100 was relatively simple. Samples would be aged at five elevated temperatures. The maximum aging time was to be no longer than three months. Following the suggestion of Gillen and Mead,[2] samples would be removed from the oven and tested at four times equally spaced on a logarithmic time scale. For a three-month study, this meant testing at 3, 9, 28, and 91 days aging at each temperature. In addition to these four samples for each oven, a fifth was added to be opened weekly for testing and then returned to the oven. This fifth sample was to be used to provide data on aging by the more common approach of

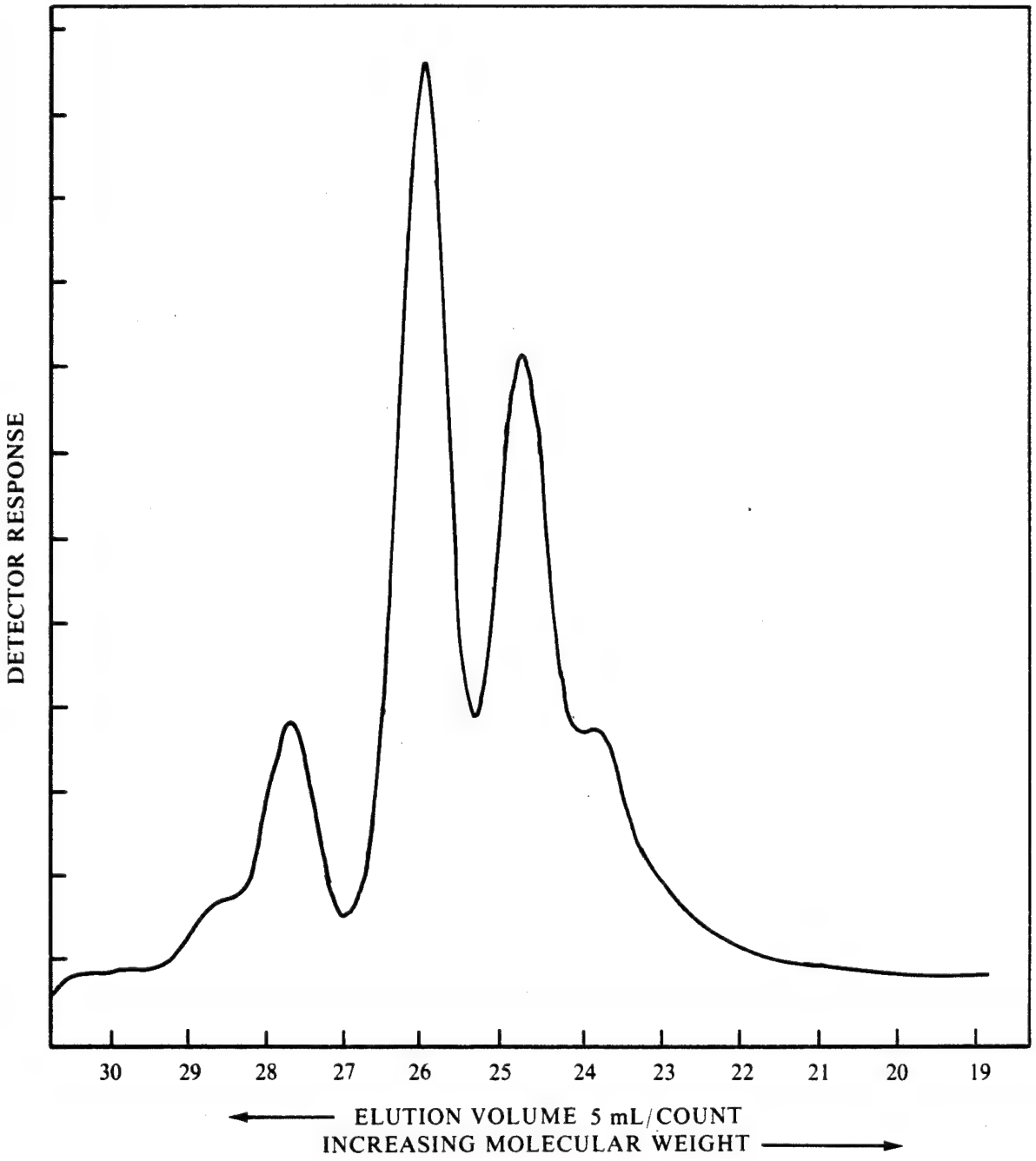


Figure 1. Gel Permeation Chromatograph of Unaged Resin

equally spaced tests on a linear time scale. Because this fifth sample would be repeatedly exposed to laboratory air and humidity, it was recognized from the start that its aging might differ somewhat from the other four, which would remain unopened until aging was complete.

Since the objective of the study was to predict shelf-life of the GE-100 at cold storage (∿5°C) for at least 10 years from aging data taken at higher temperatures for only three months, temperature selection was important. In the absence of any information to the contrary, Arrhenius-like behavior must be assumed. This means that the rate of change (aging) of the resin is assumed to be an exponential function of the reciprocal of the absolute temperature and a parameter called the activation energy (Ea). Stated formally, the Arrhenius relation is:

$$k_T = Ae^{-Ea/RT}$$

where k_T is the specific rate constant for the aging process at temperature T (K), A is a constant, Ea is the activation energy in cal/mol, and R is the ideal gas constant, 1.987 cal/mol deg. The activation energy (Ea) is generally a function of the type of rate-limiting step which controls the aging process. For example, the thermoxidation of organic materials will usually have an activation energy in the range of 20 to 30 kcal/mol, whereas a process or reaction which is diffusion-controlled will frequently have an Ea in the 5 to 15 kcal/mol range. Table 1 shows the equivalent age in years at 5°C which would result from three months of accelerated aging at several higher temperatures, for aging processes with activation energies of 10, 15, and 20 kcal/mol. Simple linear functionality with respect to time was assumed (Appendix).

Table 1 indicates that if the aging process has an activation energy of at least 20 kcal/mol, aging the resin the equivalent of at least 10 years at 5°C could be accomplished in three months at temperatures below 50°C. However, if (Ea) is 10 kcal/mol or less, considerably higher aging temperatures would be required. A sample of the GE-100 resin was aged for two weeks at 85°C. A comparison of the viscosity, epoxide equivalent, and gel permeation chromatograms before and after suggested that the aging process was homo-polymerization. This was indicated by the increase noted in viscosity, epoxide equivalent, and molecular weight. Since polymerization in a viscous medium is likely to be a diffusion-controlled process, a low activation energy might be expected. Thus temperatures of 50, 70, 85, 100, and 120°C were chosen for the aging study. Table 2 shows the time-temperature schedule for the samples to be tested on a logarithmic time scale. Table 3 gives the time-temperature schedule for the one sample at each temperature that was to be tested weekly on a linear time scale.

Aging Parameters

The quantitative properties of the resin chosen as aging parameters for this study were epoxide equivalent and kinematic viscosity.

Table 1. Equivalent Age in Years at 5°C Storage After Three Months Accelerated Aging at T_x

T_x (°C)	E=10 (kcal/mol)	E=15 (kcal/mol)	E=20 (kcal/mol)
25	0.84	1.55	2.84
50	3.12	11.0	38.8
75	9.54	88.9	364
100	25.1	252	2528
125	58.7	899	13770

Quantitative measurements are essential if the prediction of resin properties as a function of time is desired. Epoxide equivalents were determined by a modification of the method of Jay[3], which involves the titration of the epoxy groups with perchloric acid in the presence of tetraethylammonium bromide in glacial acetic acid. Kinematic viscosities were determined using a Canon Ubbelohde viscometer. The temperature of the viscometer was maintained at 35 ±0.05°C by a constant temperature bath. The unit of measurement of kinematic viscosity is the stoke $[L^2T^{-1}]$.

In addition to these two quantitative parameters, gel permeation chromatography (GPC), was used as a somewhat more qualitative tool to follow the aging process. A Waters GPC instrument using four Styragel columns of 250, 100, and 60 Å pore diameter was employed for the gel permeation chromatograms. The object of these measurements was to observe changes in molecular weight and molecular weight distribution of the resin during thermally accelerated aging.

The baseline properties of the resin were carefully determined prior to the inititation of thermal aging. Table 4 gives the average values and standard deviation of the epoxide equivalent and kinematic viscosity of the unaged material. The gel permeation chromatogram of the resin has already been presented in Figure 1.

Experimental Procedure and Results

Aging parameter measurements (kinematic viscosity and epoxide equivalent) were made on the aged samples on the same day they were removed from the aging ovens. Selected gel permeation

Table 2. Samples Tested on a Log Time Scale

	(Unopened Until Testing)			
Temperature (°C)	3 days	9 days	28 days	91 days
120	1A	2A	3A	4A
100	6B	7B	8B	9B
85	11C	12C	13C	14C
70	16D	17D	18D	19D
50	21E	22E	23E	24E

chromatograms were usually determined at a later time (up to 2 weeks), the assumption being that the samples did not change significantly in that time at room temperature. The kinematic viscosities shown in Tables 5 and 7 are the average of five measurements on each aged sample. The epoxide equivalents in Tables 6 and 8 are the average of three titrations per sample.

It quickly became obvious that while the viscosity data on the aged sample were very reproducible, the epoxide equivalent determinations were considerably less precise. In some cases two or even three sets of triplicate titrations were required to obtain data with satisfactory average values and standard deviations. This problem was partly resolved by more careful attention to the end point indicator color and by better control of the laboratory temperature. In addition, beginning with the nine-day aged samples, a redetermination of the epoxide equivalent of the unaged resin was performed each time the aged samples were analyzed. These data provided a pseudo "internal standard," again based on the assumption that the epoxide equivalent of the resin did not change measurably in three months at room temperature. The average epoxide equivalent values and standard deviation for these "internal standard" titrations are shown in Table 9. These values are an indication of the ability to obtain reproducible results with this somewhat difficult titration method.

Gel permeation chromatograms were obtained for all of the unopened aging samples (1A-4A, 6B-9B, 11C-14C, 16D-19D, 21E-14E), and for the weekly opened samples at 91 days aging (5A, 10B, 15C, 20D, and 25E). Figures 2 through 5 illustrate the progressively increasing average molecular weight of the unopened samples aged at 100°C. Figure 6 shows the extreme degree of polymerization that occurred after 91 days at 120°C.

Table 3. Samples Tested on a Linear Time Scale

°C	(Opened Weekly) (Time in Days) 3	10	17	24	31	38	45	52	59	66	73	80	87	91
120	5A													5A
100	10B													10B
85	15C													15C
70	20D													20D
50	25E													25E

Table 4. Baseline Properties of Unaged GE-100

Property	Average	Standard Deviation
Kinematic Viscosity (centistokes at 35°C)	65.93	±0.132
Epoxide Equivalent (g/equiv)	151.6	±0.225

Analysis of Results

The data in Tables 5 through 8 and the GPC results in Figures 2 through 6 indicate clearly that the aging process of the GE-100 resin equivalent is homo-polymerization. The increases observed with time and temperature in viscosity, epoxide equivalent, and the average molecular weight are all consistent with this interpretation. The increase in epoxide equivalent also shows that the epoxy groups are involved in the polymerization reaction. The detailed chemical mechanism of the reaction, however, cannot be ascertained solely from viscosity, epoxide equivalent, and GPC data. Fortunately, a detailed knowledge of chemical mechanism is not necessarily required for characterizing the aging process quantitatively in order to predict future property changes.

At least two methods are available for quantitatively analyzing the experimental results. One is the method described by Gillen and Mead[2] in which the aging parameter is plotted versus the logarithm of time for the results at each temperature. From the plot, acceleration factors are determined which permit the superposition of the results at the higher temperatures on those found at the lowest temperature. The logarithm of the acceleration factors is then plotted versus the reciprocal of the absolute temperature in order to obtain the activation energy for the aging process. This method is better suited to an aging study where the degree of aging or degradation is approximately the same at each temperature. The lower temperatures require the longer aging times. Since this project was designed to be completed in three months, it does not lend itself to analysis by this method, because there is insufficient overlap of the degree of aging at the five temperatures.

The second method is the more common approach to seeking a parametric function of the aging parameter which adequately describes the changes observed versus time (Appendix). This function can then be used to analyze the results and derive rate constants at each temperature. The Arrhenius relation may then be applied and an activation energy calculated. A knowledge of the rate constants

Table 5. Viscosities of Samples Aged on a Log-Time Scale (Unopened)

	Viscosity (centistokes at 35°C)				
Days	120°C	100°C	85°C	70°C	50°C
0	65.9	65.9	65.9	65.9	65.9
3	75.7	70.5	68.2	67.0	66.0
9	96.1	78.1	72.5	68.6	66.5
28	192.4	97.5	82.8	74.3	68.0
91	12,149.9	181.6*	111.7	90.8	72.9

*Aging time for last 100°C data point was at 89 days.

and the activation energy permits an extrapolation to lower temperatures where the prediction of the aging parameter is required. This is the method used for the data in Tables 5 through 8.

It was found that the viscosity data could be made adequately linear by plotting the natural logarithm of viscosity versus time. The plots for the two sets of viscosity data are shown in Figures 7 and 8. The parametric function for the viscosity versus time is then:

$$\text{Ln } \nu_t = \text{Ln } \nu_o + k_T t$$

or

$$\nu_t = \nu_o e^{k_T t}$$

where ν_t is the kinematic viscosity at aging time t, ν_o is the viscosity of the unaged starting material, and k_T is the specific rate constant at temperature T. It should be noted in Figure 7 that although the Ln ν versus time plots are very linear at 50, 70, 85, and 100°C, there is an upward deviation away from linearity at 120°C at viscosities above approximately 250 centistokes (~31 days at 120°C aging). However, this viscosity level is not likely to be achieved in 10 years at 4.4°C or even at room temperature, unless the activation energy is

Table 6. Epoxide Equivalent of Samples Aged on a Log-Time Scale (Unopened)

	Epoxide Equivalent ($g/equiv^{-1}$)				
Days	120°C	100°C	85°C	70°C	50°C
0	151.6	151.6	151.6	151.6	151.6
3	154.4	152.8	152.2	151.1	- - -
9	159.8	154.9	152.8	152.0	151.3
28	176.7	159.7	156.5	154.0	151.7
91	269.6	175.9*	163.5	158.9	153.6

* Aging time for last 100°C data point was 89 days.

very low. Thus, for this analysis, only the data at 120°C up to 31 days aging were used. At the lower four temperatures all the data were used.

The epoxy equivalent data were found to be linear when plotted versus time, and are shown in Figures 9 and 10. The parametric function for epoxy equivalent versus time can thus be written as:

$$E_t = E_o + k_T t \qquad (4)$$

where E_t is the epoxy equivalent at aging time t, E_o the epoxy equivalent of the unaged starting material, and k_T the specific rate constant at temperature T. As in the plotted viscosity data, the epoxy equivalent data at 120°C deviate upward from linearity after 31 days. Again, only the data at 120°C up to 31 days were used in the analysis. As before, all the data at the lower four temperatures were employed.

The viscosity data and epoxy equivalent data were fitted by a least squares linear regression analysis to Equations 2 and 4, respectively, in order to obtain the rate constants and correlation coefficients (r^2, a goodness of fit parameter) at each temperature. The results are given in Tables 10 through 14.

Tables 10 through 13 show that the linear fit of the data in most cases is excellent and in all cases can be considered satisfactory. In general the rate constants for the samples exposed

Table 7. Viscosities of Sample Aged on a Linear Time Scale (Opened Weekly)

	Viscosity (centistokes at 35°C)				
Days	120°C	100°C	85°C	70°C	50°C
0	65.9	65.9	65.9	65.9	65.9
3	75.2	70.8	68.5	67.1	66.1
10	100.6	79.2	73.1	69.1	66.5
17	125.3	86.8	77.4	71.2	66.9
24	164.9	95.8	82.5	73.3	67.5
31	226.5	107.2	87.5	75.3	68.2
38	319.0	118.2	92.6	77.4	68.5
45	477.3	130.1	98.9	79.7	69.4
52	734.8	143.3	105.0	81.7	69.8
59	1186.6	158.0	112.1	83.9	70.4
66	2030.5	167.9**	119.8	86.4	71.1
73	3821.4	187.0**	128.4	89.1	71.4
80	9479.0	211.6**	138.3	91.9	72.2
87	*	240.9**	149.4	97.2	72.9
91	*	268.7**	158.7	98.8	73.2

*Sample too viscous to test.
**Oven failed for two days. Last five aging times are 64, 71, 78, 85, and 89 days at 100°C.

weekly to laboratory air and humidity are somewhat larger than those for samples that remained unopened at the aging temperatures.

A knowledge of the rate constant at the five temperatures permits the application of the Arrhenius equation to find the constant A and the activation energy Ea. Taking logarithms of both sides, Equation 1 becomes:

$$\text{Ln } k_T = -E/R \frac{1}{T} + \text{Ln } A. \qquad (5)$$

Thus a plot of Ln k_T versus the reciprocal of the absolute (Kelvin) temperature should give a line with slope -Ea/R and intercept Ln A. Such plots for the two sets of viscosity rate constants and two sets of epoxy equivalent rate constants are shown in Figures 11

Table 8. Epoxide Equivalent of Samples Aged on a Linear Time Scale (Opened Weekly)

	Epoxide Equivalent ($g/equiv^{-1}$)				
Days	120°C	100°C	85°C	70°C	50°C
0	151.6	151.6	151.6	151.6	151.6
3	154.9	153.1	152.7	151.8	151.4
10	161.6	155.9	154.2	152.8	151.5
17	166.8	158.0	155.0	153.0	151.8
24	172.7	160.2	156.1	153.9	151.4
31	174.4	161.4	157.3	154.3	151.5
38	189.2	164.8	159.8	155.1	152.3
45	198.6	167.0	161.6	156.4	152.8
52	209.9	169.6	163.1	157.0	153.0
59	223.2	172.3	164.2	157.7	152.9
66	235.5	174.4**	166.6	158.7	153.7
73	254.4	176.0**	168.6	159.6	- - -
80	265.4	182.4**	170.7	160.3	154.0
87	*	185.5**	171.4	161.2	154.2
91	*	185.7**	172.7	162.3	154.6

*Sample would not dissolve.
**Oven failed for two days. Last five aging times at 100°C, are 64, 71, 78, 85, and 89 days.

through 14. The solid line in each figure is the result of the least squares linear regression analysis of the rate constant data. The values for A, Ea, and the correlation coefficient resulting from each data set are shown in Table 14.

The close agreement among the four values obtained for the activation energy (Ea) is a strong indication that the aging parameters chosen, viscosity and epoxide equivalent, are measuring the progress of the same chemical reaction(s). This measurement is an important requirement for any attempt to predict future properties of the resin.

Table 9. Epoxide Equivalent of Unaged Resin Versus Time

Time (Days)	Average Epoxide Equivalent (g/equiv)	Standard Deviation
9	150.5	0.460
10	151.5	0.105
17	151.4	0.246
24	151.2	0.080
28	151.4	0.059
31	151.2	0.206
38	151.5	0.263
45	151.4	0.084
52	151.7	0.035
55	151.6	0.259
66	151.8	0.050
73	151.5	0.084
80	151.8	0.038
87	151.7	0.313

The information necessary to predict kinematic viscosity and epoxide equivalent of the resin as a function of temperature and time is now available. The rate constants at the desired temperature can be calculated from the Arrhenius equation and the values of A and Ea given in Table 14. The constants can then be used in Equations 2 and 4 to calculate the viscosity and epoxide equivalent as a function of storage time at that temperature. For example, the rate constant for the change in viscosity for storage at 4.4°C in closed containers is:

$$k_{4.4} = Ae^{-Ea/RT} = 1.819 \times 10^{5} e^{\frac{-12,180}{(1.987)\ (277.6)}}$$

$$k_{4.4} = 4.67 \times 10^{-5}\ \text{days}^{-1} \qquad (6)$$

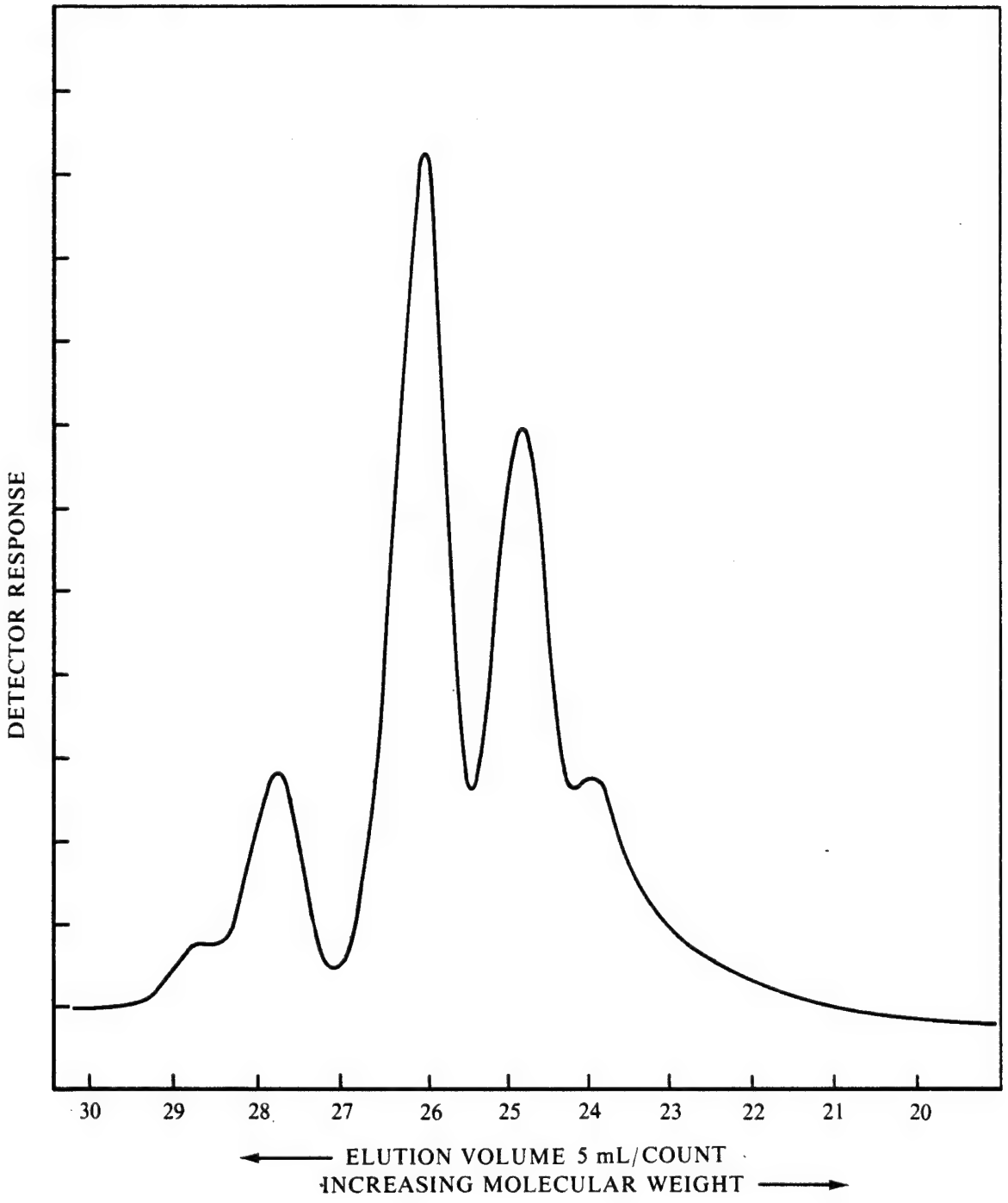


Figure 2. Gel Permeation Chromatograph of Resin Aged Three Days at 100°C

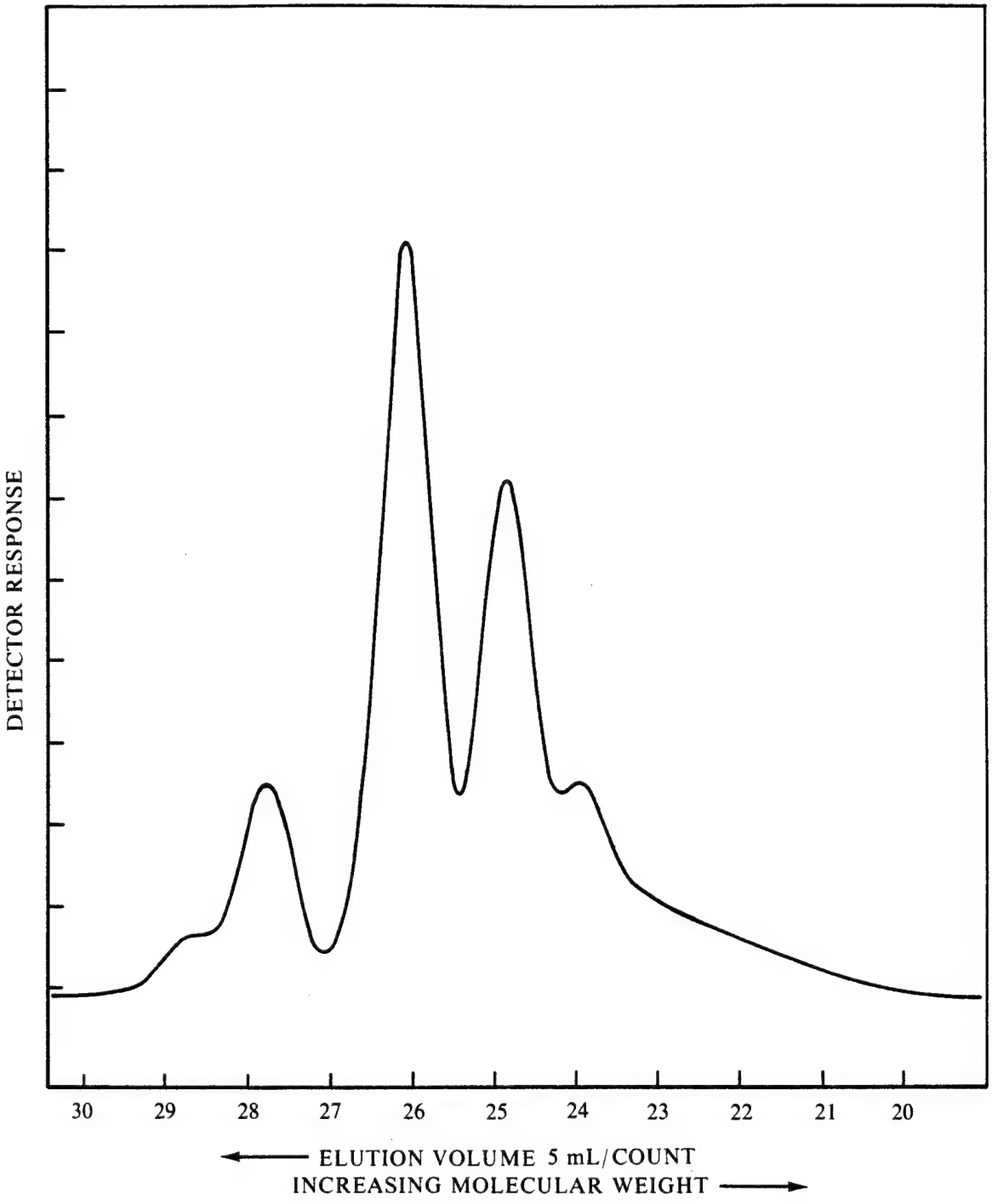


Figure 3. Gel Permeation Chromatograph of Resin Aged Nine Days at 100°C

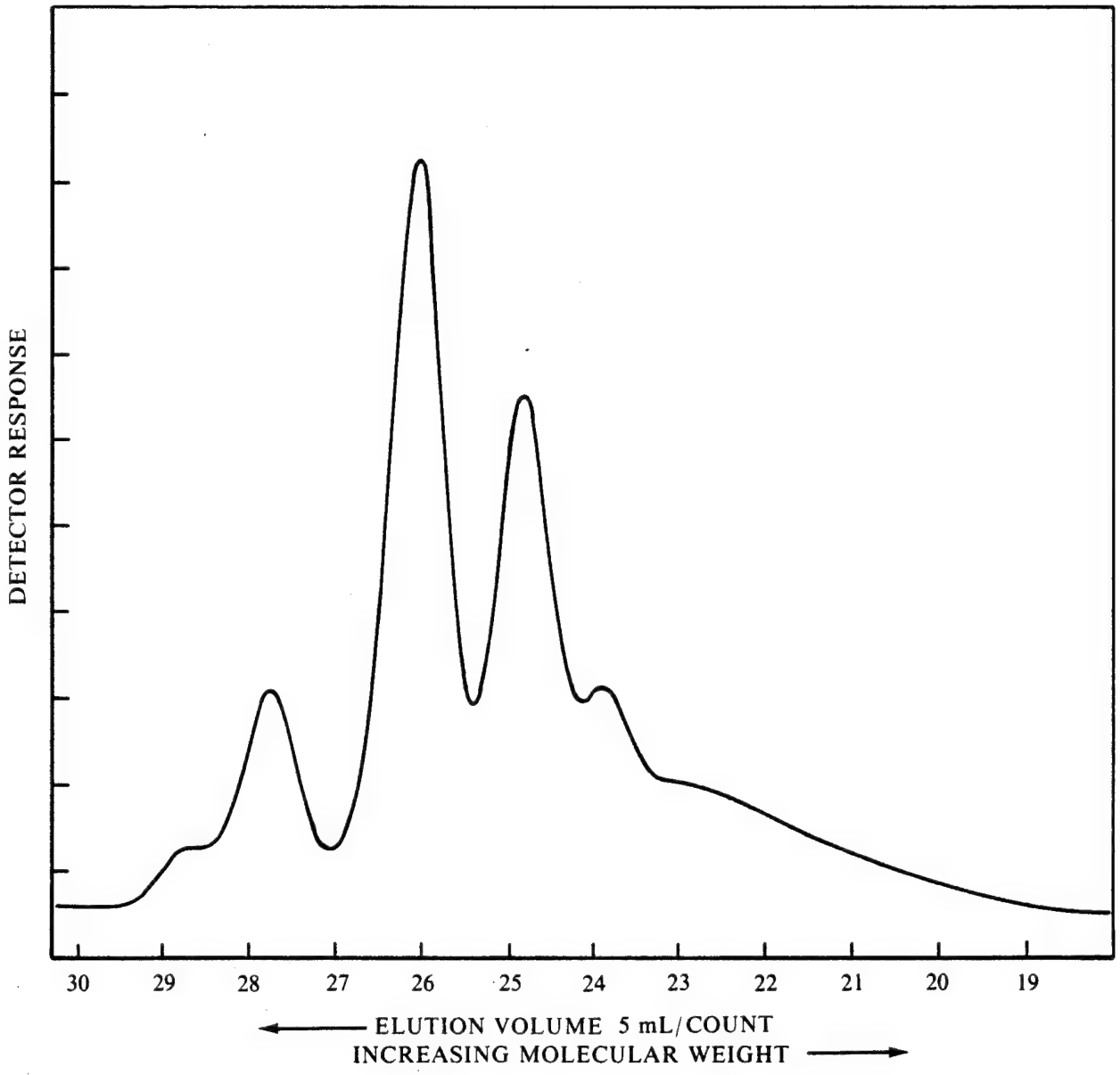


Figure 4. Gel Permeation Chromatograph of Resin Aged 28 Days at 100°C

This value can then be substituted into Equation 2,

$$\text{Ln } \nu_t \ (4.4°C) = \text{Ln } \nu_o + k_{4.4}t = 4.188 + 4.67 \times 10^{-5}t \quad (7)$$

or

$$\nu_t \ (4.4°C) = 65.9 \ e^{4.67 \times 10^{-5}t} \quad (8)$$

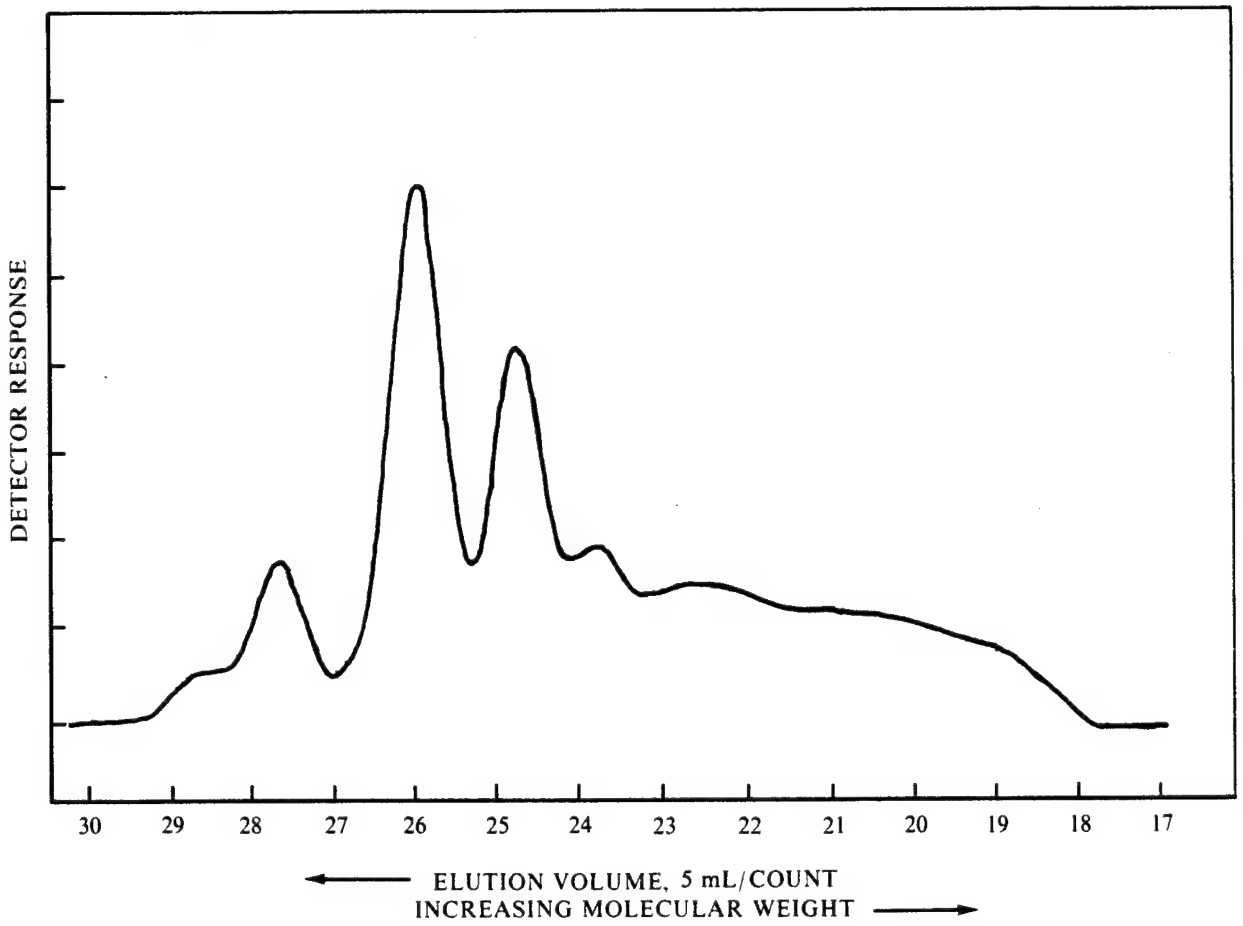


Figure 5. Gel Permeation Chromatograph of Resin Aged 89 Days at 100°C

where t = the storage time in days, and ν_t is the kinematic viscosity as determined at 35°C after storage at 4.4°C. Using this method, the expected viscosities and epoxide equivalents for storage in both frequently opened and closed containers were calculated for storage temperatures of 4.4 and 25°C. These are shown in Tables 15 and 16 for storage times up to 4000 days (10.9 years).

The data in the two tables show that while periodic exposure to ambient air and humidity have some influence on the rate of aging, the effects are not dramatic.

The activation energies obtained also permit a time-temperature superposition of the actual experimental data onto the two anticipated storage conditions. That is, one can calculate the time required to achieve the same degree of aging at 4.4 or 25°C that

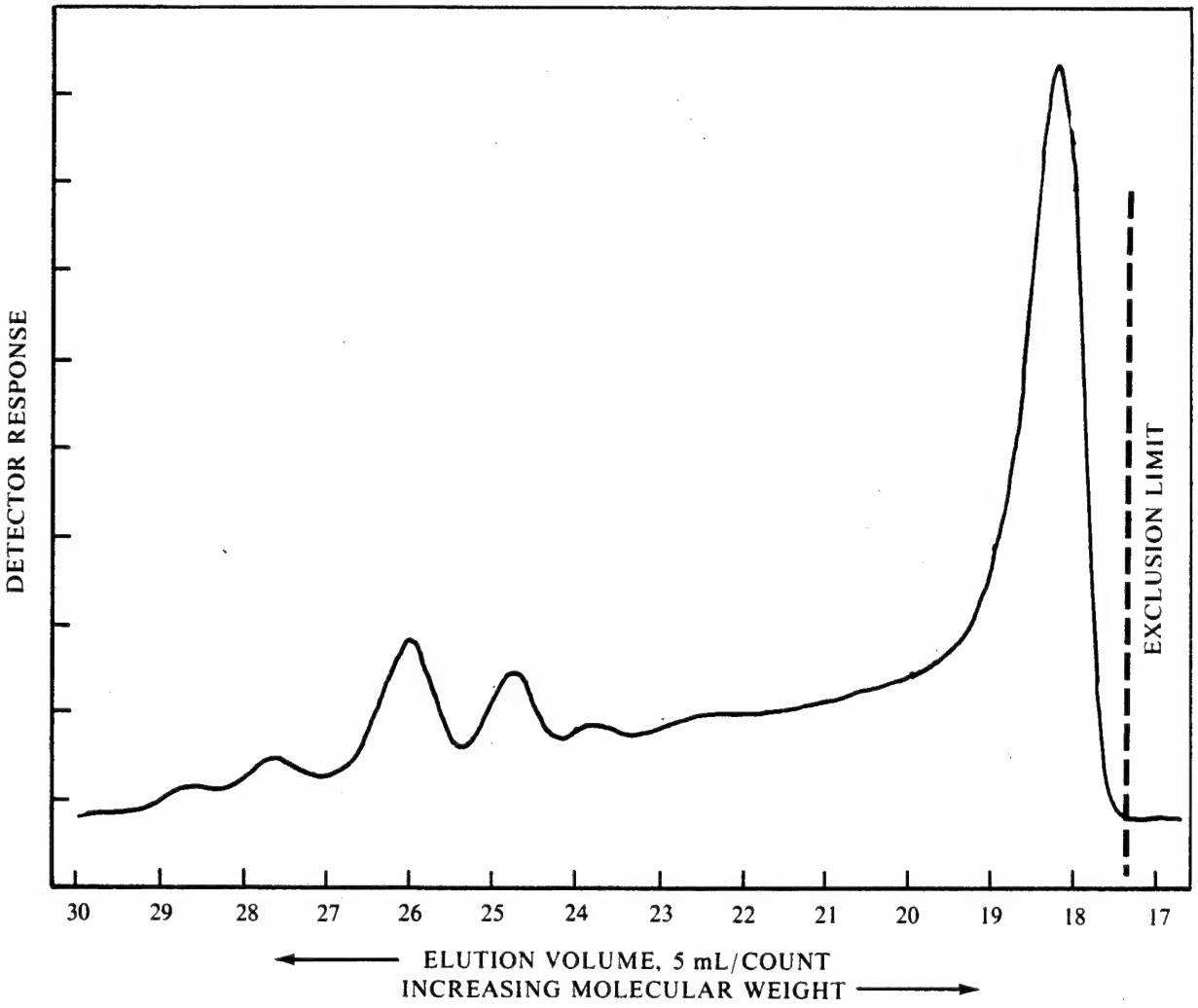


Figure 6. Gel Permeation Chromatograph of Resin Aged 91 Days at 120°C

was actually obtained at the higher aging temperatures. These calculations were of interest because one objective of the study was to formulate and test samples of Ablefoam Number 5 prepared from resin aged the equivalent of 10 to 11 years at both 4.4 and 25°C.

If the degree of aging of two samples maintained at different temperatures is equivalent, then the measurable properties of the two must also be equivalent. Thus, to calculate the effective age at 25°C storage of a sample actually aged one day at 120°C, using the epoxide equivalent as the measurable property, the property is equated at the two temperatures:

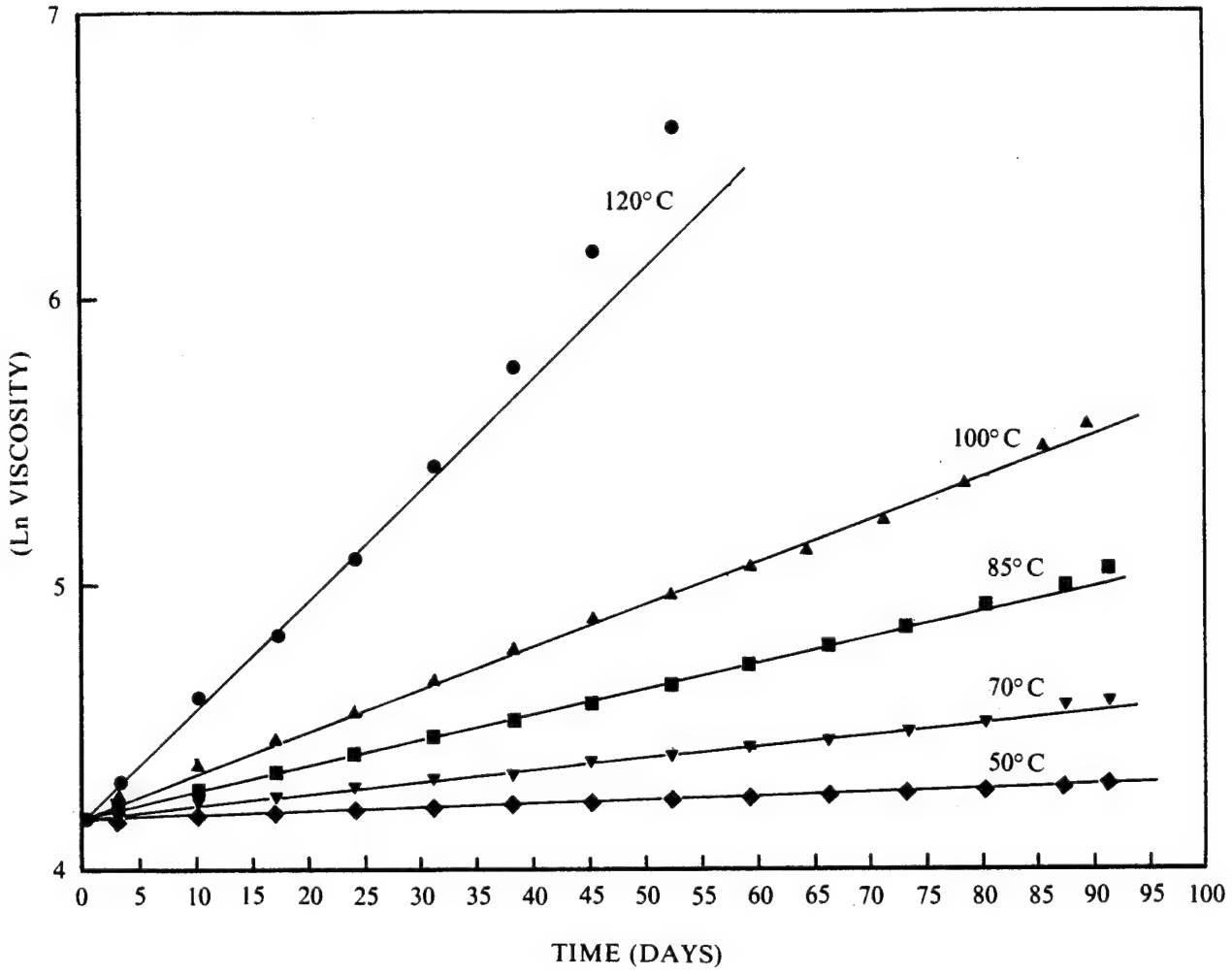


Figure 7. Logarithm (e) of Viscosity Versus Aging Time for Samples Opened Weekly

$$E(1 \text{ day at } 120°C) = E\ (t_{25} \text{ days at } 25°C) \tag{8}$$

Using Equation 4 and the Arrhenius expression for the rate constant at each temperature yields,

$$E_o + Ae^{\frac{-Ea}{R}\left(\frac{1}{393.16}\right)} .1 = E_o + Ae^{\frac{-Ea}{R}\left(\frac{1}{298.16}\right)} .t_{25} \tag{9}$$

which can be rearranged to

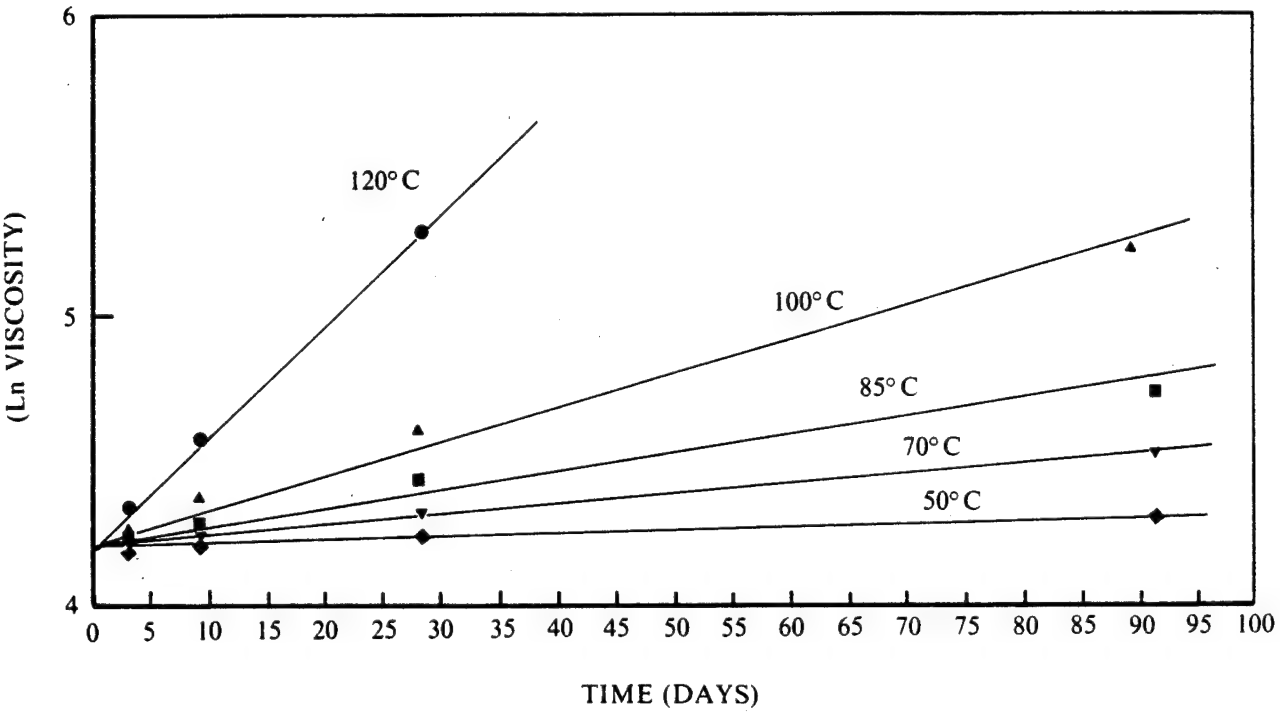


Figure 8. Logarithm (e) of Viscosity Versus Aging Time for Unopened Samples

$$t_{25}\ (\text{at } 25°C) = e^{\frac{Ea}{R}\left(\frac{1}{298.16} - \frac{1}{373.16}\right)} .1 = 156.3 \text{ days} \qquad (10)$$

The exponential term in Equation 10 is the acceleration factor for 120°C aging relative to 25°C storage. For the change in epoxide equivalent in closed containers (Ea = 12,390 cal/mol), the equation shows that each day at 120°C is equivalent to 156.3 days at 25°C. Similar calculations for time-temperature superposition at 4.4 and 25°C were made for all the data points obtained from the acceler-ated aging at the higher temperatures. A sample of the results is shown graphically in Figure 15, in which the epoxide equivalent data for opened containers are superpositioned in time on the predicted lines at 4.4 and 25°C. The legends on the graphs indicate the aging temperatures at which the data points were obtained.

Testing of Aged Resin

The changes with time in kinematic viscosity and epoxide equivalent of the resin at two storage temperatures, 4.4 and 25°C, can now

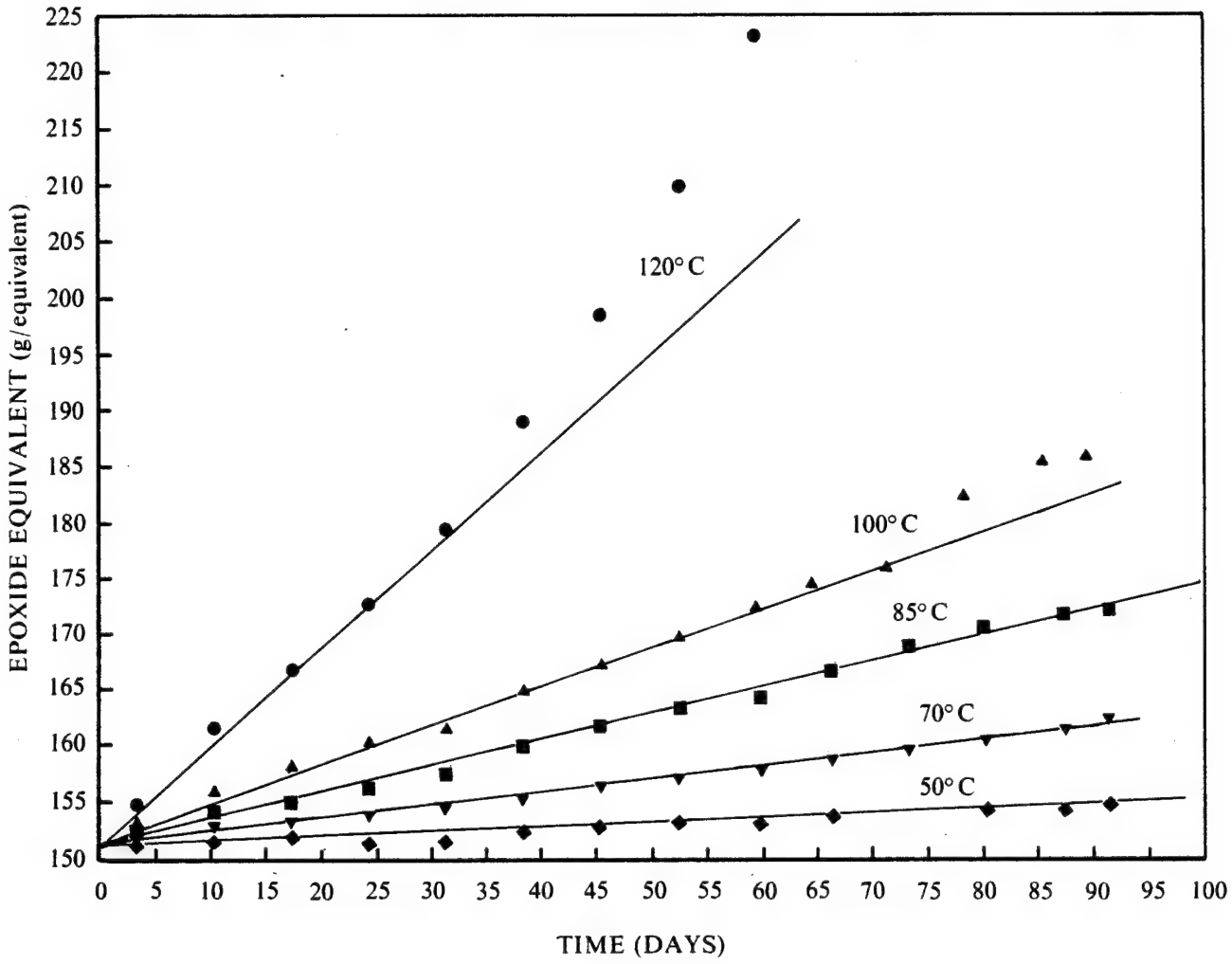


Figure 9. Epoxide Equivalent Versus Aging Time for Samples Opened Weekly

be predicted. What is not known, however, is whether resin aged 10 to 11 years at either of these temperatures can be used to prepare Ablefoam Number 5 with acceptable properties. The testing of foams prepared from resin aged the equivalent of 10 to 11 years at the two temperatures is required to provide an answer.

The time-temperature superposition calculations previously mentioned indicate that two of the samples aged in closed containers were of appropriate ages for such a test. Sample 3A (28 days at 120°C) had been aged the equivalent of 4024 days at 25°C, as indicated by the activation energy for viscosity change, or the equivalent of 4376 days as indicated by the activation energy for change in epoxide equivalent. The

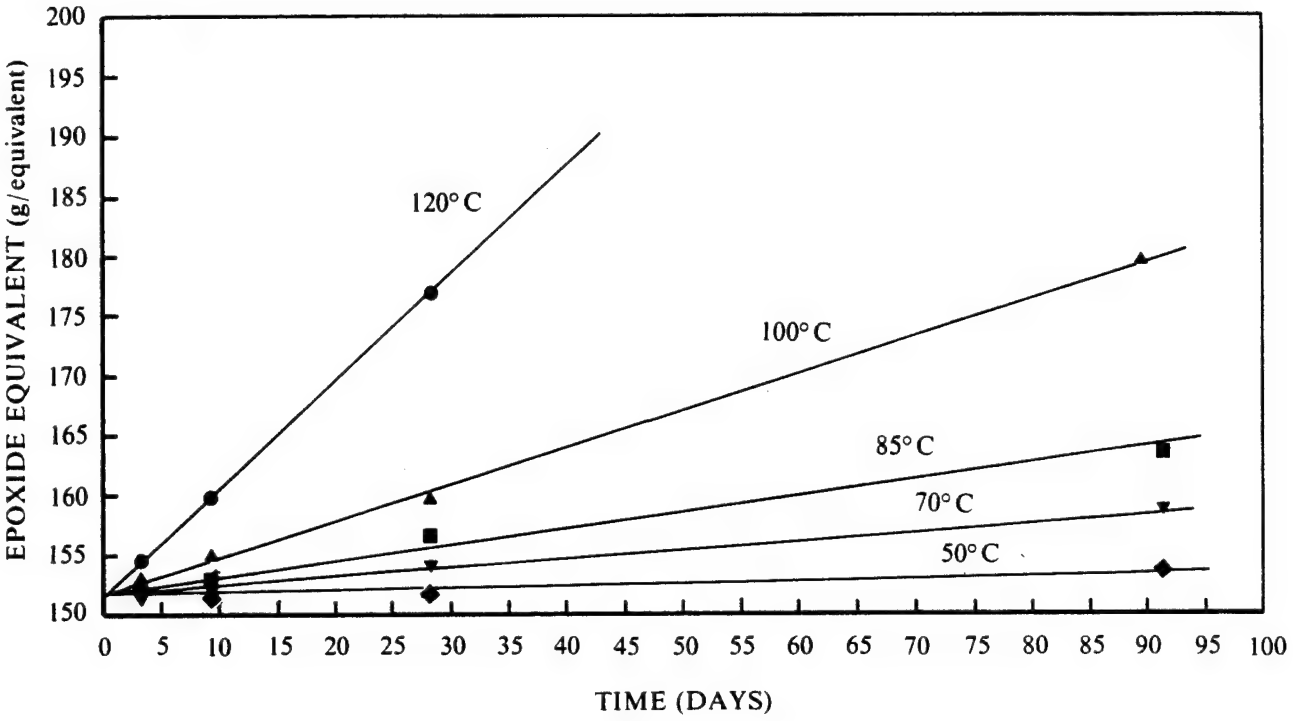


Figure 10. Epoxide Equivalent Versus Aging Time for Unopened Samples

apparent 352 day difference in equivalent age at 25°C between the two methods is simply the result of the 210 cal/mol difference between the two experimentally determined activation energies. It is interesting to note that a difference in activation energies less than 2 percent, which is experimentally insignificant, will produce a difference in calculated equivalent age of over 8 percent. Similarly, the calculations showed that sample 13C (28 days at 85°C) had been aged the equivalent of 4021 days (by viscosity) or 4374 days (by epoxide equivalent) at 4.4°C. These two samples thus have an average age of approximately 11.5 years at the storage temperatures under consideration. The fact that these samples were not opened during aging is fortunate, since this condition more nearly simulates a drum of resin stored several years before being opened for use.

Samples 3A and 13C were sent to the Ablestik Corporation to be formulated into Ablefoam Number 5 cartridges. The foam cartridges were then returned to Bendix for the manufacture of foam test samples. The foam samples for compressive strength testing were prepared and tested. Samples of foam prepared from unaged resin were also included in the test. The results of the testing are shown in Table 17. Also included in Table 17 are the minimum requirements for acceptance.

Table 10. k_T and r^2 for Viscosity Samples Tested Weekly (Opened)

Sample	Temperature (°C)	k_T (day^{-1})	r^2
5A	120	0.03884	0.998
10B	100	0.01446	0.999
15C	85	0.008926	0.999
20D	70	0.004056	0.999
25E	50	0.001169	0.997

Each value in Table 17 is the average of five samples. The results clearly show that material aged 11.5 years at either 4.4 or 25°C easily met the minimum requirements. Statistical analyses show the results from the two aged samples were not different at the 95 percent confidence level.

ACCOMPLISHMENTS

The results of this study demonstrate that the German GE-100 resin can be acquired and stored for the required 10 to 11 years without concern over degradation. The expected changes at two storage temperatures, 4.4 and 25°C, have been defined. Resin samples aged the equivalent of 11.5 years at these two temperatures have been shown to yield acceptable product. Sufficient data now exist to predict the changes in viscosity and epoxide equivalent of the resin at any other storage temperature of interest.

Table 11. k_T and r^2 for Viscosity Samples Unopened During Aging

Sample	Temperature (°C)	k_T ($days^{-1}$)	r^2
1A- 4A	120	0.03784	0.999
6B- 9B	100	0.01107	0.993
11C-14C	85	0.005621	0.983
16D-19D	70	0.003472	0.996
21E-24E	50	0.001120	0.999

Table 12. k_T and r^2 for Epoxy Equivalent Samples Tested Weekly (Opened)

Sample	Temperature (°C)	k_T ($g/equiv^{-1}$ day^{-1})	r^2
5A	120	0.8757	0.998
10B	100	0.3421	0.997
15C	85	0.2331	0.993
20D	70	0.1142	0.992
25E	50	0.03582	0.920

Table 13. k_T and r^2 for Epoxy Equivalent Samples Unopened During Aging

Samples	Temperature (°C)	kT ($g/equiv^{-1}$ $days^{-1}$)	r^2
1A- 4A	120	0.8945	0.999
6B- 9B	100	0.2629	0.999
11C-14C	85	0.1302	0.988
16D-19D	70	0.08383	0.992
21E-24E	50	0.02465	0.933

Table 14. Results of Arrhenius Analysis

Rate Constant Set	A	Ea	r^2
Viscosity (Opened)	2.862×10^5 days^{-1}	12,370 cal/mol	0.996
Viscosity (Unopened)	1.819×10^5 days^{-1}	12,180 cal/mol	0.982
Epoxy Equiv (Opened)	1.443×10^6 g equiv^{-1} days^{-1}	11,200 cal/mol	0.993
Epoxy Equiv (Unopened)	5.681×10^6 g equiv^{-1} days^{-1}	12,390 cal/mol	0.983

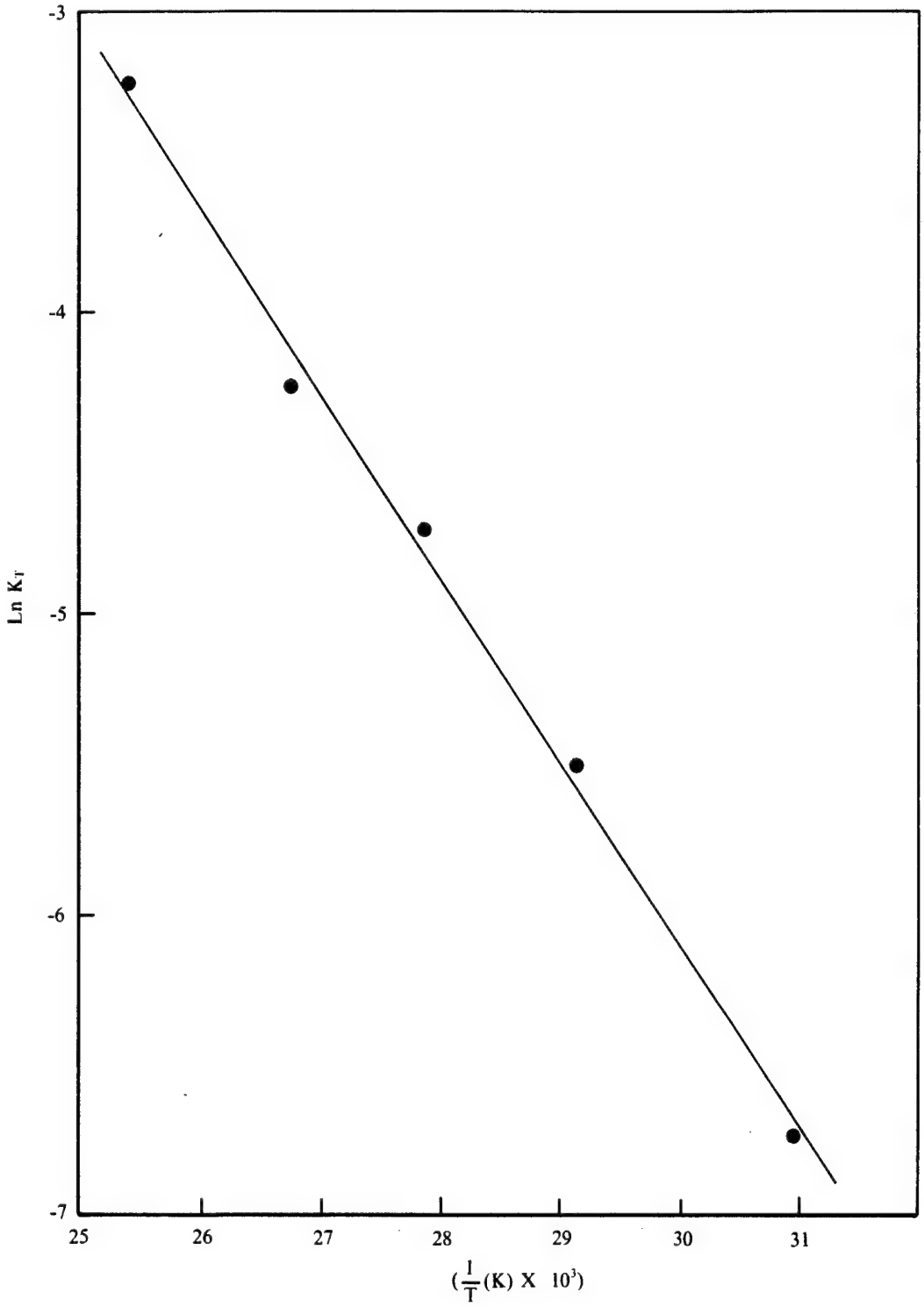


Figure 11. Arrhenius Plot of Logarithm of Rate Constant Versus Reciprocal Temperature for Viscosity Samples (Opened Weekly)

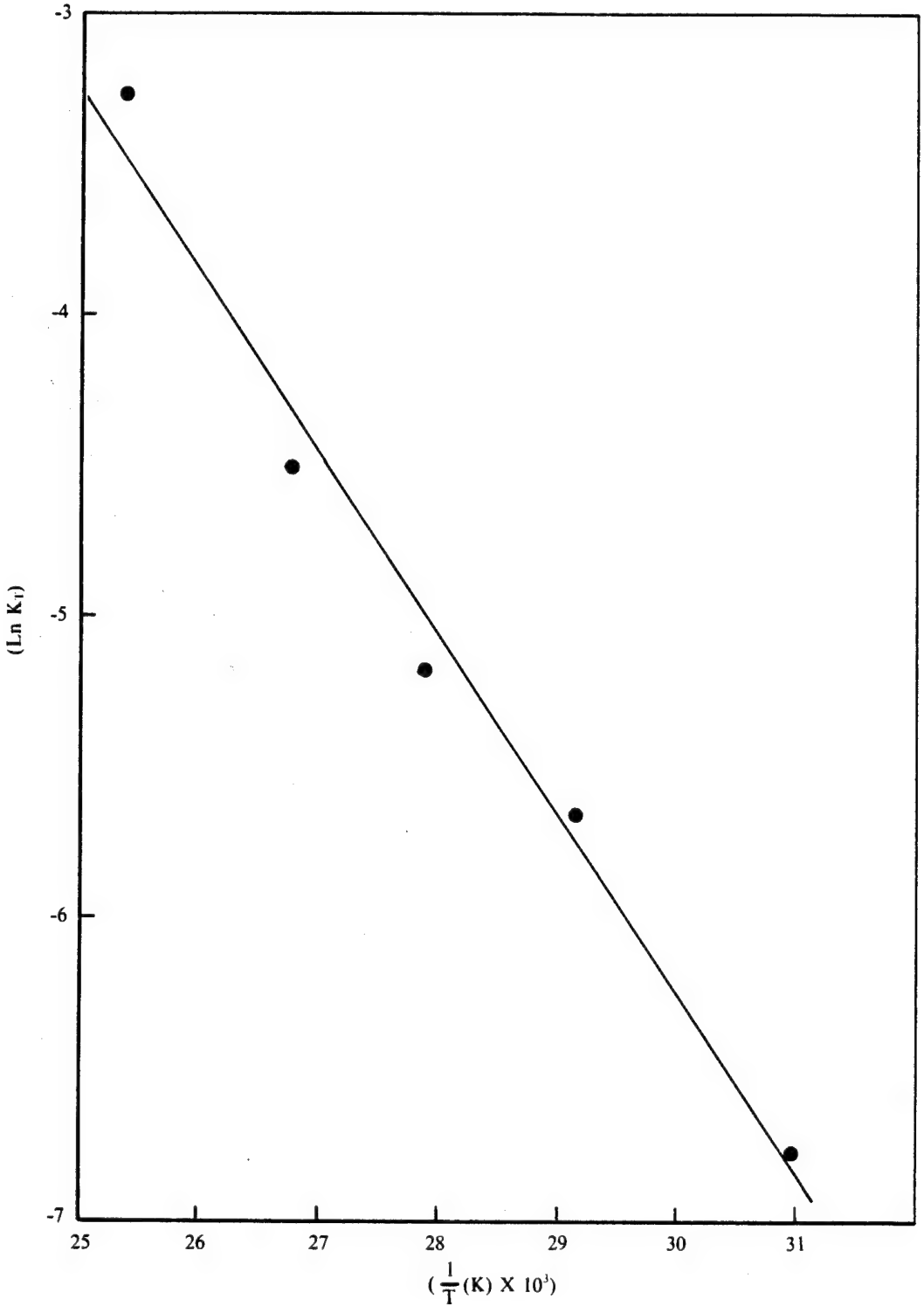


Figure 12. Arrhenius Plot of Logarithm of Rate Constant Versus Reciprocal Temperature for Viscosity Samples (Unopened)

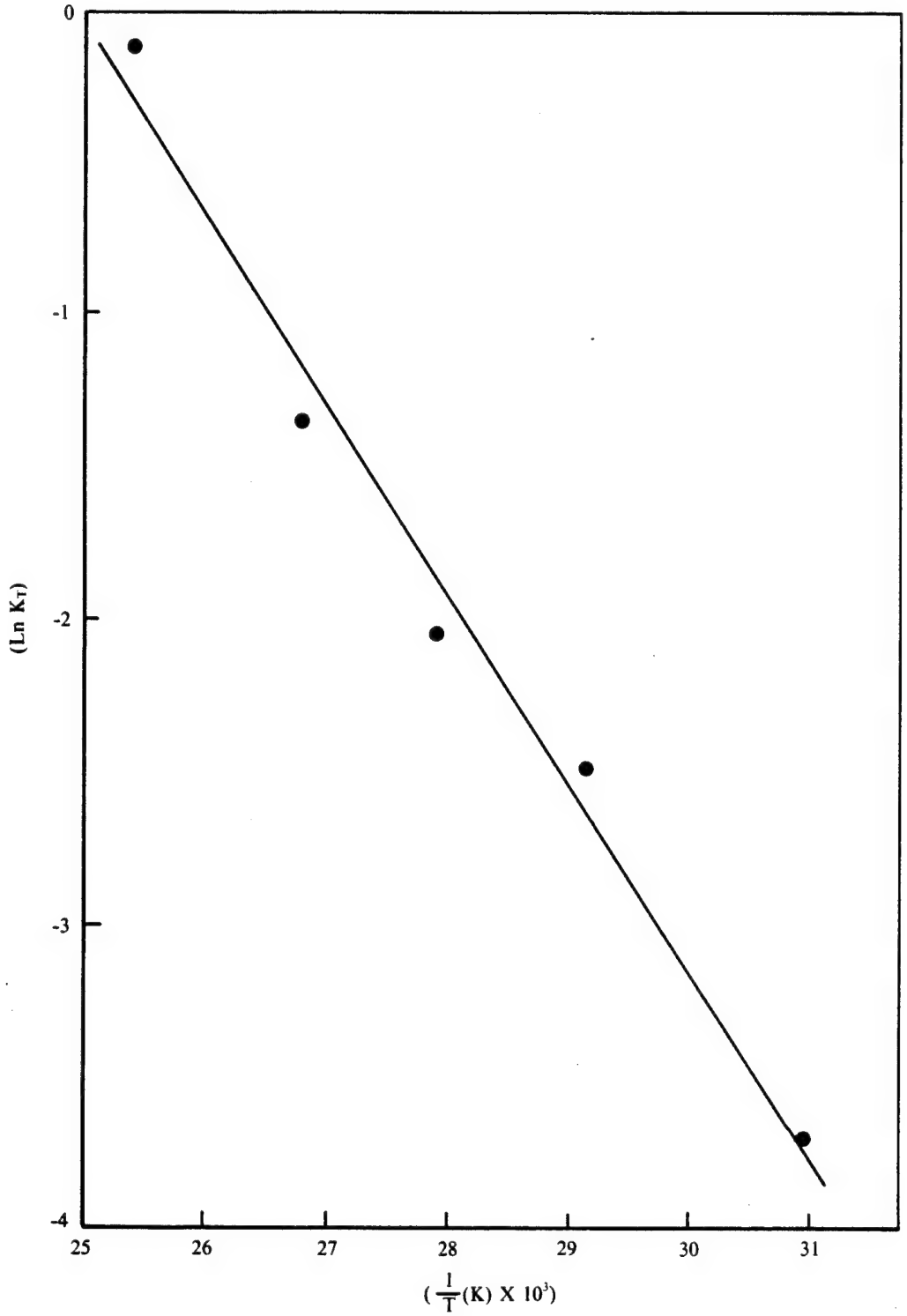


Figure 13. Arrhenius Plot of Logarithm of Rate Constant Versus Reciprocal Temperature for Epoxide Equivalent Samples (Unopened)

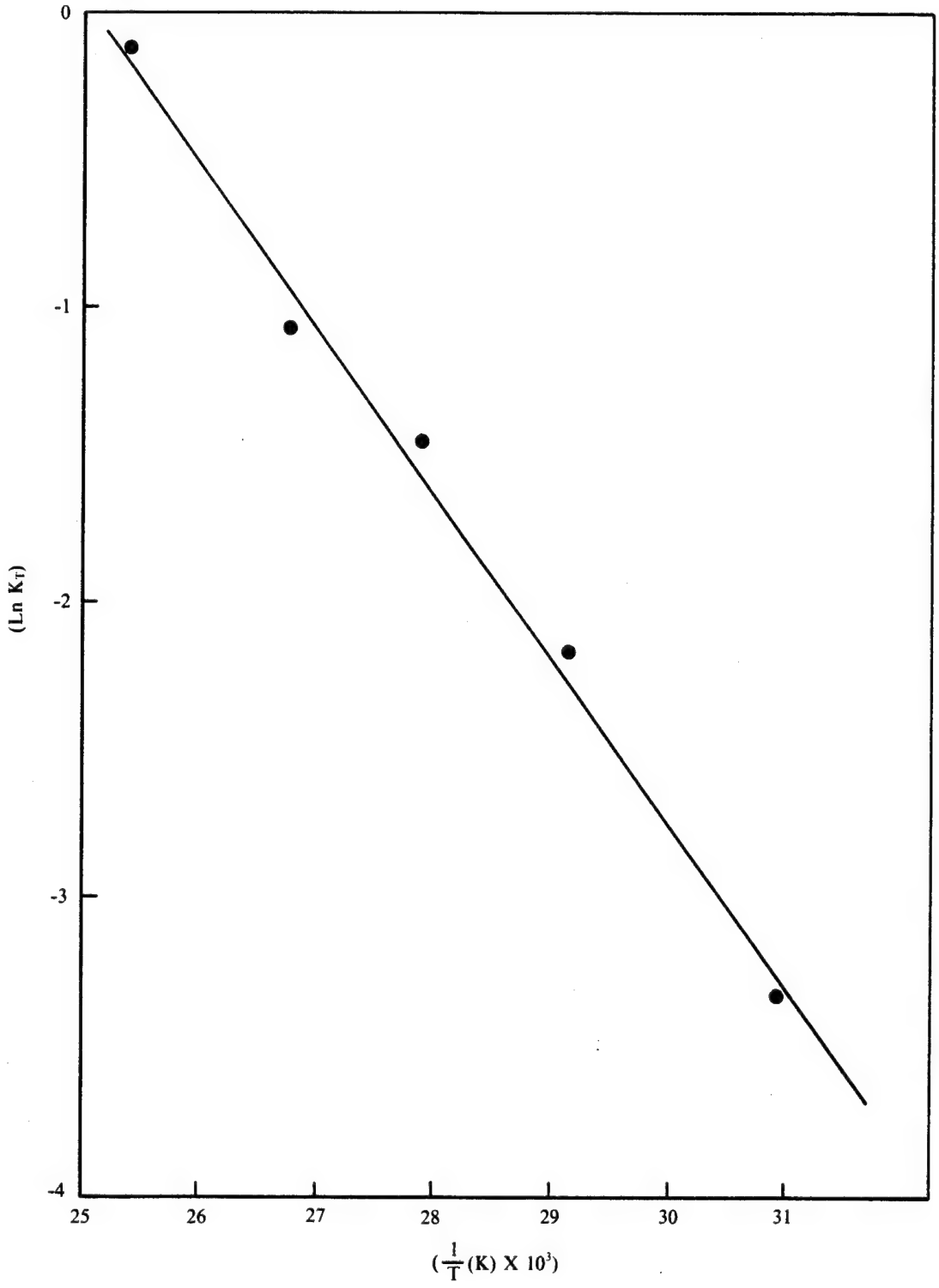


Figure 14. Arrhenius Plot of Logarithm of Rate Constant Versus Reciprocal Temperature for Epoxide Equivalent Sample (Opened Weekly)

Table 15. Predicted Viscosity and Epoxy Equivalent for Storage in Frequently Opened Containers at 4.4 and 25°C

	Viscosity (centistokes at 35°C)		Epoxy Equivalent ($g/equiv^{-1}$)	
Days	4.4°C	25°C	4.4°C	25°C
500	67.6	74.5	152.7	156.0
1000	69.4	84.3	153.8	160.4
1500	71.3	95.3	154.4	164.8
2000	73.2	107.8	155.9	169.2
2500	75.1	121.9	157.0	173.6
3000	77.1	137.8	158.1	178.0
3500	79.2	155.8	159.2	182.4
4000	81.3	176.2	160.3	186.8

Table 16. Predicted Kinematic Viscosity and Epoxide Equivalent for Storage in Closed Containers at 4.4 and 25°C

	Viscosity (centistokes at 35°C)		Epoxy Equivalent ($g/equiv^{-1}$)	
Days	4.4°C	25°C	4.4°C	25°C
500	67.4	73.3	152.1	154.0
1000	69.0	81.6	152.6	156.3
1500	70.7	90.8	153.1	168.7
2000	72.3	101.1	153.6	161.0
2500	74.0	112.5	154.1	163.4
3000	75.8	125.2	154.6	165.8
3500	77.6	139.4	155.1	168.1
4000	79.4	155.1	155.6	170.5

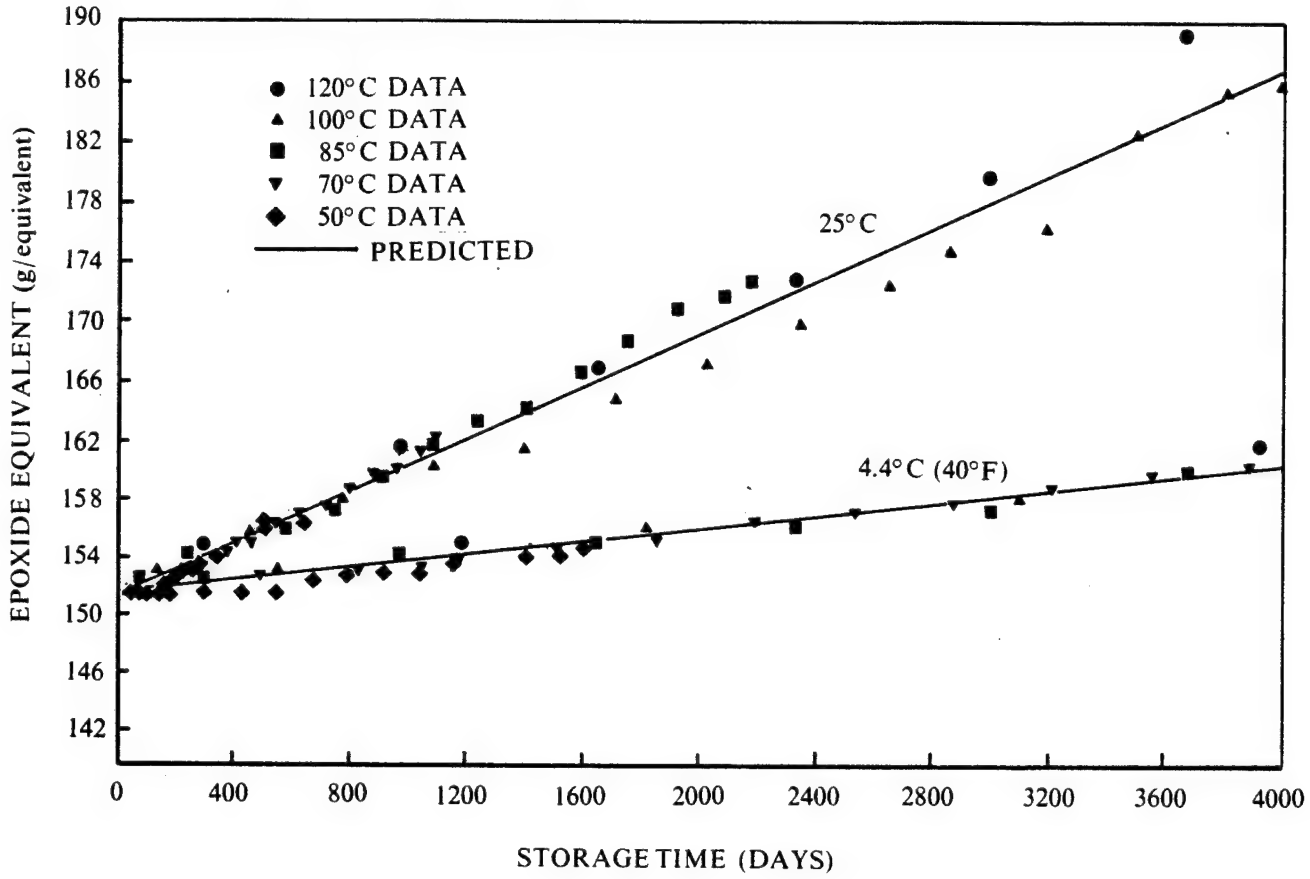


Figure 15. Time-Temperature Superposition of Epoxide Equivalent Accelerated Aging Data (Opened Weekly) Onto 4.4 and 25°C Storage Predictions

Table 17. Compressive Strength Tests on Ablefoam Number 5 Prepared From Aged and Unaged Resin

Sample	Compressive Strength, MPa	
	at 93°C	at Room Temperature
3A (11.5 years at 25°C)	3.22 (467) average 0.15 (21.8) standard deviation	7.77 (1127) 0.47 (67.8) standard deviation
13C (11.5 years at 4.4°C)	3.13 (455) average 0.32 (46.9) standard deviation	7.91 (1152) average 0.40 (57.6) standard deviation
Unaged	3.94 (573) average 0.21 (30.9) standard deviation	8.70 (1266) average 0.60 (87.9) standard deviation
Requirements	1.72 (250) minimum average	7.21 (1050) minimum average

REFERENCES

[1]Henry Lee and Kris Neville, Handbook of Epoxy Resins, New York: McGraw-Hill, 1967, (pp 2-16 and 2-18).

[2]K. T. Gillen and K. E. Mead, Predicting Life Expectancy and Simulating Age of Complex Equipment Using Accelerated Aging Techniques, Albuquerque: Sandia National Laboratories, SAND 79-1561, January, 1980 (Available from NTIS).

[3]B. Dobinson, W. Hofmann and B. P. Stark, The Determination of Epoxide Groups, New York: Pergamon Press, 1969, pp 39-40.

APPENDIX

ESTIMATING ACCELERATION FACTORS

Table 1 in the text lists the equivalent age in years at 5°C of a sample aged for three months at different temperatures, as a function of three different values for the activation energy. In preparing these estimates, two assumptions have been made. The first is that the aging or reacting system will respond to changes in temperature in accordance with the Arrhenius relation. This assumption is virtually universal in accelerated aging studies, and has received general acceptance.

The second assumption involves the measurable property or properties of the system followed quantitatively during aging, which we shall call the aging parameter(s). To make the estimates in Table 1, it is assumed that there exists some function of the aging parameter which can be expressed as a linear function of time.

That is

$$f(A.P.) = k_T t + \text{const.}$$

where t is the aging time. k_T is the specific reaction rate constant and is a function of temperature. Such linear functions are well known for chemical reactions of zero, integral, and half-integral reaction order. Thus it may generally be anticipated that if an aging process is the result of chemical reaction, such a linear function may be found.

If the degree of aging of two samples maintained at different temperatures for different lengths of time is equivalent, then their measurable properties (aging parameters) must also be equivalent. We can then write

$$f(A.P.)\ (t_1,T_1) = f(A.P.)\ (t_2,T_2)$$

where t_1 and T_1 refer to the aging time and temperature at real use conditions, and t_2 and T_2 refer to the time and temperature under accelerated aging conditions. This equality can be rewritten as:

$$k_{T_1} \cdot t_1 = k_{T_2} \cdot t_2$$

Substituting the Arrhenius relation for the rate constants then yields

$$Ae^{-Ea/RT_1} \cdot t_1 = Ae^{-Ea/RT_2} \cdot t_2$$

which rearranges to

$$t_1 = e^{\frac{Ea}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)} \cdot t_2$$

The values of t_1 (equivalent age at 5°C) shown in Table 1 were calculated by use of the above equation, assuming t_2 = 3 months and T_1 = 278.16K (5°C), and employing the several different values for accelerated aging temperature (T_2) and activation energy (Ea) indicated in the table.

BDX-613-2643

SHELF LIFE DETERMINATION OF AN EPOXY RESIN BY ACCELERATED AGING, H. M. Smith, Final, September 1981

The aging characteristics of GE-100, a German manufactured equivalent of Shell's Epon 812 epoxy resin, were determined by an accelerated aging study. The changes induced in the GE-100 by thermal aging were observed at five elevated temperatures over a period of three months. Analysis of the data permitted a prediction of the changes expected during shelf storage of the resin at 4.4, and at 25°C. Test samples of Ablefoam Number 5, prepared from GE-100 resin thermally aged the equivalent of 11.5 years at 4.4 and at

SPECIAL PROJECTS: Accelerated Aging

SHELF LIFE DETERMINATION OF AN EPOXY RESIN BY ACCELERATED AGING, H. M. Smith, Final, BDX-613-2643, September 1981

The aging characteristics of GE-100, a German manufactured equivalent of Shell's Epon 812 epoxy resin, were determined by an accelerated aging study. The changes induced in the GE-100 by thermal aging were observed at five elevated temperatures over a period of three months. Analysis of the data permitted a prediction of the changes expected during shelf storage of the resin at 4.4, and at 25°C. Test samples of Ablefoam Number 5, prepared from GE-100 resin thermally aged the equivalent of 11.5 years at 4.4 and at

SHELF LIFE DETERMINATION OF AN EPOXY RESIN BY ACCELERATED AGING, H. M. Smith, Final, BDX-613-2643, September 1981

The aging characteristics of GE-100, a German manufactured equivalent of Shell's Epon 812 epoxy resin, were determined by an accelerated aging study. The changes induced in the GE-100 by thermal aging were observed at five elevated temperatures over a period of three months. Analysis of the data permitted a prediction of the changes expected during shelf storage of the resin at 4.4, and at 25°C. Test samples of Ablefoam Number 5, prepared from GE-100 resin thermally aged the equivalent of 11.5 years at 4.4 and at

25°C, met all WR specifications. The results indicate that the GE-100 resin has a shelf-life exceeding 11 years at cold storage and at ambient conditions.

25°C, met all WR specifications. The results indicate that the GE-100 resin has a shelf-life exceeding 11 years at cold storage and at ambient conditions.

25°C, met all WR specifications. The results indicate that the GE-100 resin has a shelf-life exceeding 11 years at cold storage and at ambient conditions.